



TITLE:

Studies on the Correlation between
Chemical Constitution and Insectidal Activity
of Halogenated Aromatic Compounds. (V) :
Studies on the Chlorinated Compounds of
BHC

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CITATION:

Hamada, Masayuki ...[et al]. Studies on the Correlation between Chemical Constitution and Insectidal Activity of Halogenated Aromatic Compounds. (V) : Studies on the Chlorinated Compounds of BHC. 京都大学化学研究所報告 1950, 23: 79-80

ISSUE DATE:

1950-12-30

URL:

<http://hdl.handle.net/2433/74170>

RIGHT:

indicated not only that the chain had a plane zigzag configuration, but also that all the hydroxyl groups lay on the same side of the zigzag plane. However, it has been shown recently by C. W. Bunn²⁾ that the observed repeat distance might be equally compatible with a molecular structure in which hydroxyl groups were randomly placed in left- and right-hand positions because hydroxyl groups might replace hydrogen atoms at random on a carbon chain without destroying crystallinity.

For the explanation of X-ray diffraction of polyvinyl alcohol it is not necessary to assume such a stereochemical irregularity of this molecule³⁾. A particular, irregular arrangement of molecules with hydroxyl groups regularly (alternatively) placed in left- and right-hand positions accounts in a satisfactory way for the diffraction pattern. It is only necessary to assume that the second molecular chain in a unit cell is displaced from the first 1.26 Å (a length of a carbon atom in the zigzag chain) in the direction of fiber axis randomly up- and down-wards. It can be easily seen that the both displacements may equally likely occur. Although atomic positions given by Bunn fit also for this arrangement, the following parameters give somewhat better agreement with the observed intensities: C (of CH₂) at 0.243 a, 0.250 b, 0.065 c, C (of CH) at 0.293 a, 0.750 b, 0.217 c half of the oxygen atom at 0.166 a, 0.750 b, 0.420 c and the other half at 0.466 a, 0.750 b, 0.480 c. Dimensions of the unit cell are a=7.83 Å, b=2.52 Å, c=5.53 Å $\beta=87^\circ$.

1) R. C. L. Mooney, J. Amer. Chem. Soc., **63**, 2828 (1941).

2) C. W. Bunn, Nature **161**, 102 (1948).

3) C. W. Bunn, Nature **159**, 161 (1947).

73. Studies on the Correlation between Chemical Constitution and Insectidal Activity of Halogenated Aromatic Compounds. (V)

Studies on the Chlorinated Compounds of BHC.

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(Takei Laboratory)

When chlorine gas was introduced into carbon tetrachloride solution of pure γ -BHC under the direct sunlight, γ -BHC was chlorinated very easily. In our experiments, greater part of γ -BHC was chlorinated by 30 minutes reaction at 40°C and unreacted γ -BHC was not detected after 4.5 hours reaction (Reaction A). The reaction products were very viscous oil and fractionated under vacuum. From the results of elemental analysis and polarographic observation, these products were found chiefly to be the mixtures of hepta- and octa-chlorocyclohexanes. On the other hand, isomers of hepta- and octa-chlorocyclohexanes were synthesized purely

and the physical properties were determined.

Then we tested the insecticidal activities of the following materials against houseflies (*Musca domestica* L.): Four fractions of Reaction A (F-1~4); α -heptachlorocyclohexane (mp. 153-4°); γ -heptachlorocyclohexane (84-5°); *o*-octachlorocyclohexane (149°); β -*p*-octachlorocyclohexane (262°); γ -BHC.

The modified turn table method was adopted and the testing results are shown in the Table.

Toxicity of Chlorinated Compounds of BHC against Houseflies.
(Kill in 24 hours, per cent)

mg/cc	γ -BHC	F-1	F-2	F-3	F-4	α -hepta	γ -hepta	<i>o</i> -octa	β - <i>p</i> -octa
0.00025	34.3	—	—	—	—	—	—	—	—
0.0005	41.8	—	—	—	—	—	—	—	—
0.001	51.1	—	—	—	—	—	—	—	—
0.002	62.5	—	—	—	—	—	—	—	—
0.125	—	45.5	49.5	38.9	21.8	62.7	48.1	75.2	22.5
0.25	—	55.3	59.7	50.2	30.9	74.8	59.2	78.5	44.6
0.5	—	68.0	72.9	61.8	37.5	83.8	64.0	84.3	61.9
1.0	—	82.4	86.1	72.9	42.6	90.7	72.6	88.0	—

In these tests only γ -BHC is found very effective while chlorinated products of γ -BHC and other highly chlorinated compounds all ineffective. So in the technical preparation it is preferable to remove γ -BHC from the reaction system which might be produced from benzene and chlorine, as soon as possible in order to avoid further chlorination.

74. Studies on the Molecular Structures of BHC and its Related Compounds. (II)

On the Molecular Structure of γ -Monochlorobenzene Hexachloride.

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In the previous reports (Oiwa, T., et al: *Botyu-Kagaku*, 14, 42 (1949); *ibid.*, 15, 32 (1950)) we published the details of our investigations about the molecular structures of BHC and its related compounds. In this paper we report the molecular configuration of γ -monochlorobenzene hexachloride (mp. 85-86°).

Two grams of γ -monochlorobenzene hexachloride were chlorinated in the 150 grams of carbon tetrachloride containing 6 grams of chlorine under the light for 1 hour. After the removal of the solvent 2.16 grams of slightly yellowish oily matter was obtained. Then from this matter 0.15 gram of colorless crystals